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Basis set consistent revision of the S22 test set of noncovalent interaction energies

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The S22 test set of interaction energies for small model complexes [Phys. Chem. Chem. Phys. **8**, 1985 (2006)] has been very valuable for benchmarking new and existing methods for noncovalent interactions. However, the basis sets utilized to compute the CCSD(T) interaction energies for some of the dimers are insufficient to obtain converged results. Here we consistently extrapolate all CCSD(T)/complete basis set (CBS) interaction energies using larger basis sets for the CCSD(T) component of the computation. The revised values, which we designate S22A, represent the most accurate results to date for this set of dimers. The new values appear to be within a few hundredths of 1 kcal mol^{-1} of the true CCSD(T)/CBS limit at the given geometries, but the former S22 values are off by as much as 0.6 kcal mol^{-1} compared to the revised values. Because some of the most promising methods for noncovalent interactions are already achieving this level of agreement (or better) compared to the S22 data, more accurate benchmark values would clearly be helpful. The MP2, SCS-MP2, SCS-CCSD, SCS(MI)-MP2, and B2PLYP-D methods have been tested against the more accurate benchmark set. The B2PLYP-D method outperforms all other methods tested here, with a mean average deviation of only 0.12 kcal mol^{-1}. However, the consistent, slight underestimation of the interaction energies computed by the SCS-CCSD method (an overall mean absolute deviation and mean deviation of 0.24 and −0.23 kcal mol^{-1}, respectively) suggests that the SCS-CCSD method has the potential to become even more accurate with a reoptimization of its parameters for noncovalent interactions. © *2010 American Institute of Physics*. [doi:10.1063/1.3378024]

I. INTRODUCTION

It is now well recognized that the proper characterization of noncovalent interactions requires the use of high-level *ab initio* methods including electron correlation effects. This has been shown extensively for the difficult case of the benzene dimer.[1–5] The coupled-cluster theory through perturbative triples, CCSD(T),[6] has emerged as the most accurate method that can be computationally afforded for modest sized systems and is considered the "gold standard" for chemical accuracy.[7] As research continues on larger noncovalent systems, it is very helpful to test the methods against available CCSD(T) data. Unfortunately these data are somewhat limited due to the $O(N^7)$ scaling of the CCSD(T) method, where N is proportional to the system size. For noncovalent complexes where CCSD(T) computations are tractable, recent studies have tested various approximate methods that show promising results.[8–14]

Excellent work by Hobza and co-workers[15–18] provided several key databases of CCSD(T) noncovalent interaction energies. Among the most popular is the S22 test set, which contains 22 dimers of various types (H-bonded, dispersion dominated and mixed) and system sizes (from water dimer to adenine-thymine complexes).[16] It has become increasingly common to benchmark existing and new methods against the S22 test set;[19–27] some methods are even being parametrized or adjusted based on reducing the error compared to the S22 interaction energies.[28–30]

Despite the high accuracy of the initial S22 CCSD(T) interaction energies, the basis sets used vary between complexes.[16] As has become customary in such studies, estimates of the CCSD(T) complete basis set (CBS) limit were obtained using an additive approximation, $E^{\mathrm{CBS}}_{\mathrm{CCSD(T)}} \approx E^{\mathrm{CBS}}_{\mathrm{MP2}} + (E^{\mathrm{small}}_{\mathrm{CCSD(T)}} - E^{\mathrm{small}}_{\mathrm{MP2}})$, where $E^{\mathrm{small}}_{\mathrm{CCSD}(T)} - E^{\mathrm{small}}_{\mathrm{MP2}}$ is a "coupled-cluster correction," ΔCCSD(T), evaluated in a small or medium-sized basis. No diffuse functions were used for the CCSD(T) computations in the S22 set except for the well documented T-shaped and parallel-displaced benzene dimers.[3,31] The MP2 interaction energies were extrapolated with the cc-pVQZ and cc-pV5Z basis sets, or the cc-pVTZ and cc-pVQZ basis sets, depending on the size of the complex (diffuse functions were included only in a few cases). The inconsistent use of basis sets (driven by necessity in the 2006 computations) was noted previously by Marchetti and Werner[23] while testing explicitly correlated wave function methods for the computation of intermolecular interactions. Furthermore, for the larger complexes such as conformations of adenine-thymine and indole-benzene, only double-ζ quality basis sets, without diffuse functions, were used for the

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CCSD(T) correction. Recently, potential energy curves for 20 complexes of the S22 test set were computed at the CCSD(T)/CBS limit, in which the ΔCCSD(T) terms were consistently evaluated with the aug-cc-pVDZ basis set.[32]

Unfortunately, as pointed out by Janowski and Pulay,[33] double-ζ quality basis sets are not always sufficient to converge the coupled-cluster correction. Marchetti and Werner[27] worked to increase the basis sets for CCSD(T) computations of the S22 complexes. However, they neglected the diffuse functions on the hydrogens and only computed the interaction energies for the smaller complexes of the S22 test set. The CCSD(T)/aug-cc-pVTZ interaction energies have been obtained for the stacked methyl adenine-methyl thymine complex[34] and two uracil dimer conformations.[4] Both studies suggested that the interaction energies for the larger complexes of the S22 test set could change as much as a few to several tenths of 1 kcal mol^{-1} when evaluating the ΔCCSD(T) term with the larger aug-cc-pVTZ basis set. CCSD(T) computations on the benzene dimer using full or truncated aug-cc-pVQZ basis sets also demonstrate that the ΔCCSD(T) term can change by around one-tenth of 1 kcal mol^{-1} from the aug-cc-pVDZ values.[14,33,35]

II. THEORETICAL METHODS

This study consistently extrapolates all interaction energies of the S22 test set to the CCSD(T)/CBS limit. The MOLPRO package of *ab initio* programs[36] was used to compute most interaction energies. The largest coupled-cluster computations used NWCHEM 5.1 (Refs. 37 and 38) on the Cray XT4 "Jaguar" at Oak Ridge National Laboratory. Computations employed the aug-cc-pVXZ (X=D,T,Q) basis sets of Dunning *et al.*[39,40] and were counterpoise corrected.[41] MP2/CBS energies were computed by adding a two-point extrapolation[42] of the aug-cc-pVTZ and aug-cc-pVQZ correlation energies to the aug-cc-pVQZ reference self-consistent field (SCF) energy, denoted as (aT-aQ). To these values, a coupled-cluster correction, ΔCCSD(T), evaluated in a smaller basis was added (see below). For smaller systems, we directly extrapolated CCSD(T) correlation energies to obtain CCSD(T)/CBS(aT-aQ) interaction energies. The largest changes to the SCF component of the interaction energies when increasing from the aug-cc-pVTZ to the aug-cc-pVQZ basis sets were observed for the formic acid and formamide dimers, both by 0.09 kcal mol^{-1}. When increasing further to the aug-cc-pV5Z basis set, the SCF interaction energies for both of these dimers only changed by 0.01 kcal mol^{-1}. Similar results were previously obtained utilizing truncated versions of the basis sets by Marchetti and Werner,[23] where the SCF/aug-cc-pVQZ′ errors were not greater than 0.02 kcal mol^{-1} compared to the SCF/aug-cc-pV5Z′ results for the entire S22 test set. Thus, the SCF component of the interaction energies seems essentially converged with the aug-cc-pVQZ basis set.

Regarding the MP2/CBS estimates, it is not obvious to us which values are more reliable, the present (aT-aQ) extrapolations, or the (aQ′-a5′) extrapolations of Marchetti and Werner.[23] The latter study went up to quintuple-ζ basis sets (compared to quadruple-ζ in the present work), but it neglected the diffuse functions on hydrogen atoms, which we include here. However, there is a high level of agreement between our MP2/CBS estimates and those of Marchetti and Werner (the largest difference is 0.03 kcal mol^{-1}). For the H-bonded systems, there is a somewhat larger difference between our counterpoise-corrected and uncorrected MP2/CBS estimates (see supplemental material[43]) than one might desire, but comparison to Marchetti and Werner's MP2/CBS estimates [or the limited (aT′-aQ′) CCSD(T) extrapolations of Marchetti and Werner[27] in the case of CCSD(T)/CBS] suggests that the counterpoise-corrected values are more accurate and are essentially converged.

The coupled-cluster correction, ΔCCSD(T), was evaluated with the aug-cc-pVDZ and aug-cc-pVTZ basis sets; these results are referred to as the ΔaDZ and ΔaTZ corrections, respectively. We also estimated a more reliable ΔCCSD(T) correction as the difference between the two-point extrapolated CCSD(T) and MP2 correlation energies using the aug-cc-pVDZ and aug-cc-pVTZ basis sets; this is referred to as the Δa(DT)Z correction. All ΔCCSD(T) terms were added to the MP2/CBS(aT-aQ) energies. By comparison to larger-basis CCSD(T) computations, the quality of the Δa(DT)Z correction scheme has been shown to be highly accurate for the benzene dimer, methane-benzene, and H_2S-benzene complexes.[14] The MP2, SCS-MP2,[8] SCS-CCSD,[11] SCS(MI)-MP2,[29] and B2PLYP-D (Ref. 28) methods have been re-evaluated against the new CCSD(T)/CBS(Δa(DT)Z) results.

We have chosen to adopt the original S22 geometries. Interaction energies and geometries would change slightly upon further optimization (e.g., interaction energies would change by −0.01 and −0.08 kcal mol^{-1} for the T-shaped and parallel-displaced benzene dimers, respectively).[14] Some of the dimers that were originally optimized without diffuse functions might change somewhat more than this. However, as the primary value of the S22 test set has been in validation of theoretical binding energies rather than in comparisons to experiment, any reasonable set of geometries will suffice, and using the original geometries makes it easier to compare prior work to our revised benchmark data.

III. RESULTS

Table I shows all CCSD(T)/CBS interaction energy approximation schemes, along with fully extrapolated CCSD(T)/CBS(aT-aQ) interaction energies for the smallest complexes and the original S22 data. Comparing the fully extrapolated CCSD(T)/CBS(aT-aQ) interaction energies to the approximate extrapolations, all schemes give similar errors for the smallest complexes (ammonia, water, methane, ethene, and ethane·ethine dimers), with the ΔaDZ scheme being slightly less accurate for the hydrogen bonded cases. The Δa(DT)Z scheme, however, yields superior results for the interaction energies of the formic acid and formamide dimers; at the ΔaTZ level, the interaction energy errors are around one-tenth of 1 kcal mol^{-1}, whereas at the Δa(DT)Z level the errors are within one-hundredth of 1 kcal mol^{-1}. We further note that the interaction energies were nearly converged at the ΔaDZ level for all the mixed complexes, with

TABLE I. CCSD(T) basis set consistent interaction energies in kcal mol^{-1} for the S22 test set.

Complex	Original[a]	CBS(ΔaDZ) [b]	CBS(ΔaTZ) [c]	CBS(Δa(DT)Z) [d]	CBS[e]
			H-bonded complexes		
$(NH_3)_2$	−3.17	−3.10	−3.15	−3.17	−3.15
$(H_2O)_2$	−5.02	−4.92	−4.99	−5.02	−5.07
Formic acid dimer	*−18.61*	−18.46	−18.70	−18.80	−18.81
Formamide dimer	*−15.96*	−15.84	−16.03	−16.12	−16.11
Uracil dimer	*−20.65*	−20.42	−20.61	−20.69	···
2-pyridoxine·2-aminopyridine	*−16.71*	−16.70	−16.91	−17.00	···
Adenine·thymine WC	*−16.37*	−16.43	−16.65	−16.74	···
			Dispersion dominated complexes		
$(CH_4)_2$	−0.53	−0.53	−0.53	−0.53	−0.53
$(C_2H_4)_2$	−1.51	−1.48	−1.49	−1.50	−1.48
Benzene·CH_4	−1.50	−1.47	−1.45	−1.45	···
PD benzene dimer	*−2.73*	−2.73	−2.65	−2.62	···
Pyrazine dimer	*−4.42*	−4.33	−4.24	−4.20	···
Uracil dimer	*−10.12*	−9.83	−9.77	−9.74	···
Stacked indole·benzene	*−5.22*	−4.62	−4.60	−4.59	···
Stacked adenine·thymine	*−12.23*	−11.82	−11.71	−11.66	···
			Mixed complexes		
Ethene·ethine	−1.53	−1.50	−1.51	−1.51	−1.50
Benzene·H_2O	−3.28	−3.27	−3.28	−3.29	···
Benzene·NH_3	−2.35	−2.33	−2.32	−2.32	···
Benzene·HCN	−4.46	−4.52	−4.54	−4.55	···
T-shaped benzene dimer	−2.74	−2.75	−2.72	−2.71	···
T-shaped indole benzene	*−5.73*	−5.63	−5.63	−5.62	···
Phenol dimer	−7.05	−7.04	−7.08	−7.09	···

[a]Taken from Ref. 16. Italicized energies denote the significant changes (>0.1 kcal mol^{-1}) compared to the CBS(Δa(DT)Z) results.
[b]Estimated via an addition of the difference between MP2 and CCSD(T) correlation energies with the aug-cc-pVDZ basis set to the MP2/CBS(aT-aQ) energies.
[c]Estimated via an addition of the difference between MP2 and CCSD(T) correlation energies with the aug-cc-pVTZ basis set to the MP2/CBS(aT-aQ) energies.
[d]Estimated via an addition of the difference between MP2/CBS(aD-aT) and CCSD(T)/CBS(aD-aT) correlation energies to the MP2/CBS(aT-aQ) energies.
[e]Two-point extrapolation of the CCSD(T) correlation energies with the aug-cc-pVTZ and aug-cc-pVQZ basis sets.

differences of less than 0.04 kcal mol^{-1} when comparing to the ΔaTZ interaction energies. It is, therefore, reasonable to assume that the Δa(DT)Z interaction energies for the mixed complexes must also result in, at most, a few hundredths of 1 kcal mol^{-1} error compared to the fully extrapolated CCSD(T)/CBS(aT-aQ) interaction energies. Furthermore, compared to the CCSD(T)/CBS(aT′-aQ′) interaction energies (with truncated basis sets) for several of the test cases published by Marchetti and Werner[27] (see supplemental material[43]), and the benzene·CH_4 dimer and three orientations of the benzene dimer in our previous work,[14] the Δa(DT)Z correction also incurs only a few hundredths of 1 kcal mol^{-1} error. Having established the effectiveness of the counterpoise-corrected CCSD(T)/CBS(Δa(DT)Z) approximation scheme, we will use these values as the benchmarks in the subsequent discussion.

In general, the severity of the ΔaDZ approximation scheme errors increases as the system sizes increase for the hydrogen bonded and dispersion dominated complexes, whereas the ΔaTZ errors remain relatively constant throughout. For the hydrogen bonded complexes, the ΔaDZ approximation underestimates the interaction energy anywhere from 0.07–0.34 kcal mol^{-1}, with the worst cases being for the formic acid dimer and adenine-thymine complex. For the dispersion dominated complexes, the ΔaDZ approximation overestimates the interaction energy by as much as 0.16 kcal mol^{-1}, with the worst case being for adenine-thymine complex. The ΔaTZ absolute errors are less than 0.1 and 0.05 kcal mol^{-1} for the hydrogen bonded and dispersion dominated complexes, respectively. For the mixed complexes, both approximation schemes perform rather well with absolute errors of less than 0.05 and 0.01 kcal mol^{-1} for the ΔaDZ and ΔaTZ schemes, respectively.

The ΔaDZ scheme yields larger absolute errors with increasing system size, and the original S22 data are also less accurate for the interaction energies of the larger complexes. This is exemplified by the formic acid dimer and adenine-thymine (Watson–Crick geometry) interaction energy errors; the original S22 value is more accurate than the ΔaDZ approximation for the formic acid dimer, but is less accurate for adenine-thymine. For the original S22 data, ΔTZ and ΔDZ CCSD(T) corrections (without diffuse functions) were com-

TABLE II. interaction energy error statistics in kcal mol^{-1} for the S22A [using CCSD(T)/CBS(Δa(DT)Z) results] test set with various methods.

Test set	Original[a]	MP2[b]	SCS-MP2[b]	SCS-CCSD[c]	SCS(MI)-MP2[d]	B2PLYP-D[e]
			H-bonded complexes			
MAD[f]	0.15	0.24	1.54	0.40	0.30	0.14
MD[g]	−0.15	−0.14	−1.54	−0.40	−0.20	0.08
rms[h]	0.20	0.27	1.69	0.47	0.36	0.17
			Dispersion dominated complexes			
MAD[f]	0.25	1.69	0.55	0.23	0.37	0.12
MD[g]	0.25	1.68	−0.32	−0.22	0.19	0.02
rms[h]	0.34	2.15	0.69	0.31	0.43	0.17
			Mixed complexes			
MAD[f]	0.05	0.61	0.37	0.08	0.17	0.11
MD[g]	0.01	0.61	−0.37	−0.08	0.06	0.07
rms[h]	0.06	0.72	0.41	0.09	0.20	0.14
			Overall			
MAD[f]	0.15	0.88	0.80	0.24	0.28	0.12
MD[g]	0.04	0.76	−0.72	−0.23	0.02	0.06
rms[h]	0.45	1.05	0.96	0.54	0.58	0.40

[a]Original S22 test set from Ref. 16.
[b]CBS(aT-aQ) interaction energies.
[c]CBS(Δa(DT)Z) interaction energies.
[d]Energies evaluated with the two-point extrapolation of the correlation energies with the cc-pVTZ and cc-pVQZ basis sets taken from Ref. 29.
[e]Energies counterpoise corrected evaluated with the aug-cc-pVTZ basis taken from Ref. 28.
[f]Mean absolute deviation.
[g]Mean deviation.
[h]Root mean squared deviation.

puted for the formic acid dimer and adenine-thymine, respectively. The use of different basis sets leads to the inconsistent reliability of the original S22 data, and the neglect of diffuse functions yields absolute errors greater than the ΔaDZ approximation errors for the larger complexes. Overall, the result of consistently utilizing the Δa(DT)Z CCSD(T) correction changes 10 of the 22 interaction energies by more than 0.1 kcal mol^{-1} from the original S22 data, as indicated in Table I.

Table II presents the mean absolute deviation (MAD), mean deviation (MD), and root mean squared (rms) deviation for the MP2, SCS-MP2, SCS-CCSD, SCS(MI)-MP2, and B2PLYP-D methods, as well as the original S22 data, compared to the S22A benchmark energies. Overall, the MP2 and SCS-MP2 methods perform similarly, with MADs of 0.88 and 0.80 kcal mol^{-1}, respectively. The MP2 method outperforms the SCS-MP2 method for hydrogen bonded complexes, whereas the SCS-MP2 method outperforms the MP2 method for both dispersion and mixed complexes. The overall performance of the SCS-CCSD and SCS(MI)-MP2 methods is somewhat similar, despite the parametrization of the SCS(MI)-MP2 method for S22 test set. The SCS(MI)-MP2 method incurs similar errors for the hydrogen bonded and dispersion dominated complexes with a slightly better performance for the mixed complexes, leading to the overall 0.28 kcal mol^{-1} MAD. The SCS-CCSD method outperforms all other methods tested here for the mixed complexes but underestimates most interaction energies to yield an overall MD of −0.23 and a MAD of 0.24 kcal mol^{-1}. While this performance is quite good, a reparametrization of the SCS-CCSD method for the computation of noncovalent interactions would likely increase its accuracy and more easily justify the expense of performing CCSD computations. The most accurate method tested is the B2PLYP-D method with an overall MAD of 0.12 kcal mol^{-1}; this method has been parametrized specifically for the original S22 interaction energies. Interestingly, increasing the basis set results in much greater errors for the dispersion dominated complexes than for the H-bonded and mixed complexes when comparing the original S22 data to the revised data. This is perhaps not surprising in that polarizability (to which dispersion is related) is known to be difficult to converge with respect to basis set.

Given the very small errors exhibited by SCS-CCSD and B2PLYP-D, the usefulness of the new benchmark energies becomes apparent. The original S22 data incur an overall MAD of 0.15 kcal mol^{-1} compared to the CCSD(T)/CBS(Δa(DT)Z) interaction energies; the overall MAD of the B2PLYP-D method is less than that of the original S22 data. Furthermore, if the original S22 data are used as the benchmarks, the MADs for the hydrogen bonded and dispersion dominated complexes of the SCS-CCSD method would be 0.25 and 0.54 kcal mol^{-1}, respectively, as opposed to 0.40 and 0.23 kcal mol^{-1}, respectively. Thus the original S22 data incorrectly suggest that the SCS-CCSD method approximates hydrogen bonded complexes more accurately than dispersion dominated complexes.

IV. CONCLUSION

A small test set of noncovalent interactions, such as the S22 test set, is indeed useful for benchmarking and parametrization purposes. However, approximate methods have now reached an accuracy where higher-quality benchmark data (using consistent basis sets across the set of dimers) are necessary to allow for further improvements. Overall, the B2PLYP-D method outperforms all other approximate methods tested here, while the SCS-CCSD method outperforms all other methods for mixed complexes. We recommend the revised benchmark energies provided here, along with recent potential energy curves for small dimers,[14] for future assessment and parametrization of methods for noncovalent interactions.

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